High-Nickel Cathode Materials for High-Energy, Long-Life, Low-Cost Lithium-Ion Batteries

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Materials Science and Engineering Program

The University of Texas at Austin

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Project ID #: bat415

OVERVIEW

Timeline

- Project start date: October 2018
- Project end date: December 2021
- 40% complete

Budget

- Total project funding
  - DOE: $2,400,000
- Funding received in FY 2018
  - $0
- Funding received in FY 2019
  - $800,000
- Funding for FY 2020
  - $800,000

Barriers

- Barriers
  - Cycle and calendar life
  - Abuse tolerance
  - Storage stability
- Targets
  - Affordable, high-performance layered oxide cathodes with low or no cobalt content (≤ 50 mg Co/Wh)

Partners

- NREL, Tesla, Inc.

RELEVANCE

Overall Project Objective

- Develop high-nickel, low-cobalt cathodes that deliver a high specific energy of ≥ 600 Wh kg^{-1} at a cobalt content of ≤ 50 mg Wh^{-1}, and have a long cycle (C/3 deep discharge with ≤ 20% energy fade over 1,000 cycles) and calendar life (≥ 15 years)

Achievements in Year 1

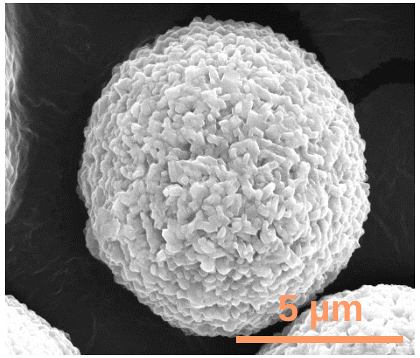
- Demonstration of an ultralow-cobalt, high-energy layered cathode in 2 Ah pouch full cells and a cobalt-free, high-energy layered cathode in 75 mAh pouch full cells

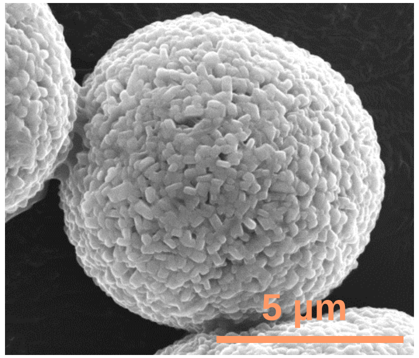
Objectives and Milestones for Year 2

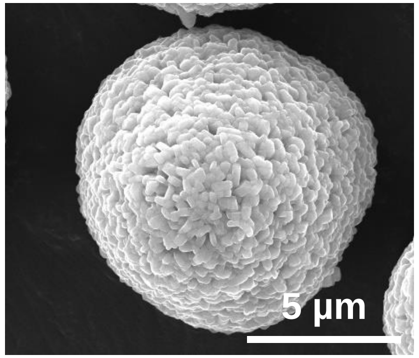
- Exploration of high-Ni $LiNi_{1-x-y}Co_yM_xO_2$ with reduced Co content (< 6%)
  - A survey of dopants on electrochemical performance, safety, and storage stability (Q1)
  - Effect of high electrode loading and calendaring on electrochemical performance (Q2)
  - Further evaluation of ALD coating on best performing $LiNi_{1-x-y}Co_yM_xO_2$ (Q3)
  - A survey of electrolyte additives on $LiNi_{1-x-y}Co_yM_xO_2$ in EC-free electrolytes (Q4)

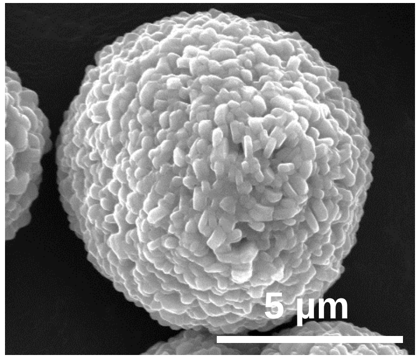
APPROACH

- **Composition Design:** Screening of metal dopants that stabilize high-nickel layered oxides in the absence of cobalt, based on coin half cell and pouch full cell performance
- **Synthesis Scale-up**: Increase the tank reactor size for co-precipitation from 10 L to 30 or 50 L. Increase the batch size for calcination from 10 – 20 g per batch to 50 – 200 g per batch
- **Surface Stabilization:** Exploration of surface treatments such as regular and ALD coating
- **Electrolyte Modification**: Exploration of functional electrolyte additives in the absence of ethylene carbonate
- **Assessment:** Evaluation in pouch full cells with commercially relevant electrode loading and porosity as well as in-depth characterization to understand the degradation mechanisms

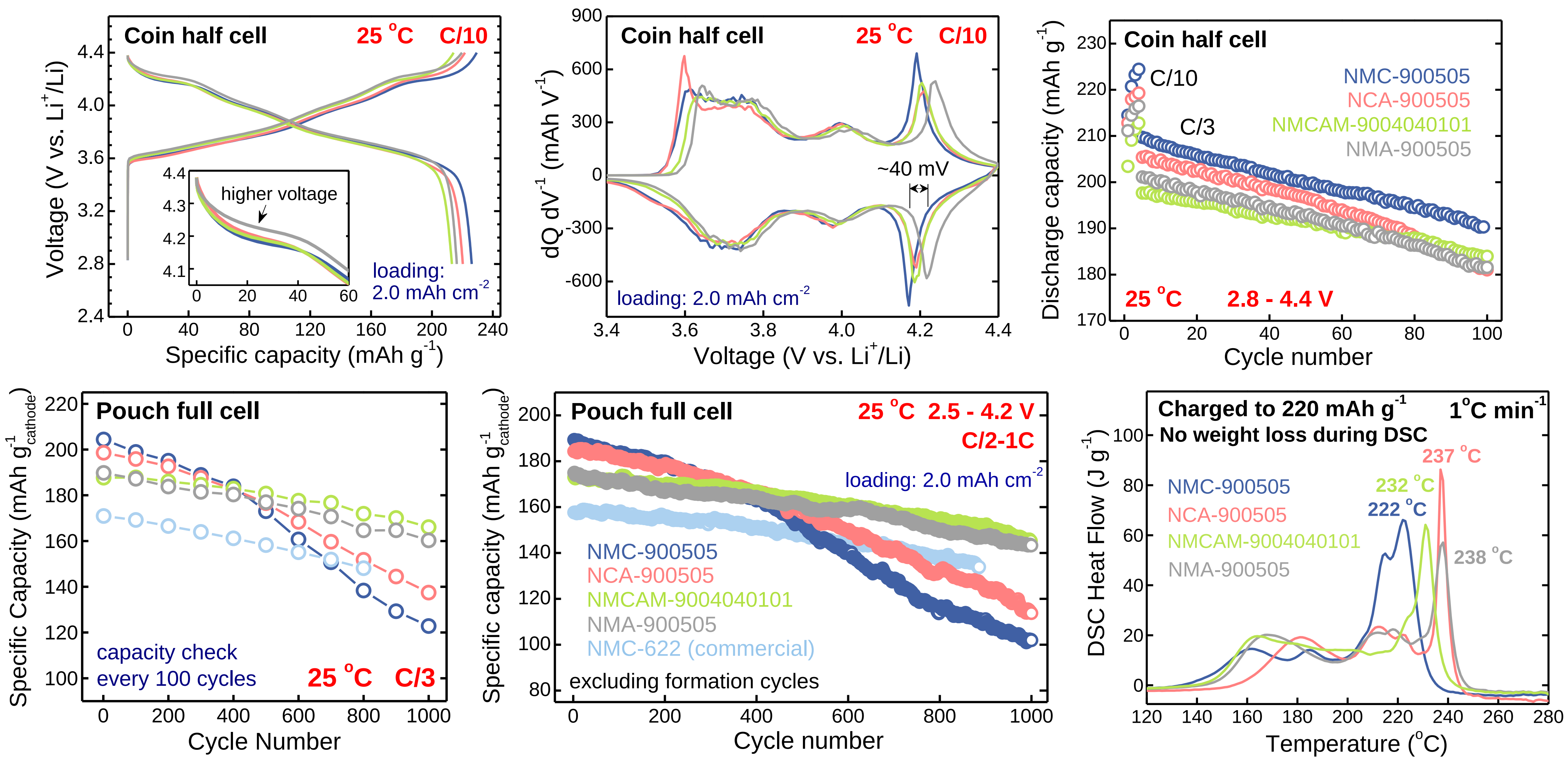






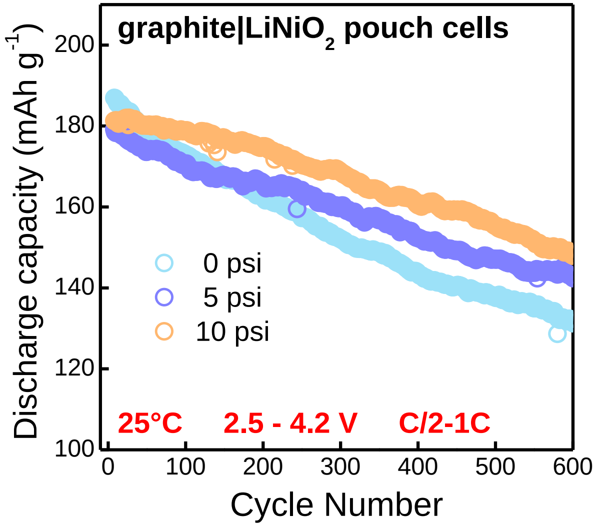


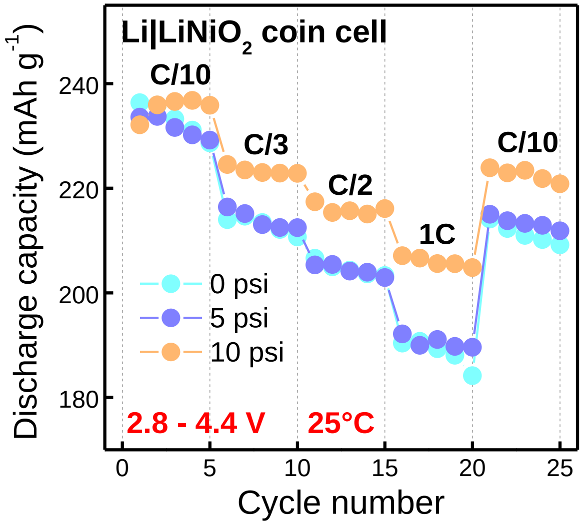
DESIGN OF HIGH-NICKEL, COBALT-FREE LAYERED CATHODES

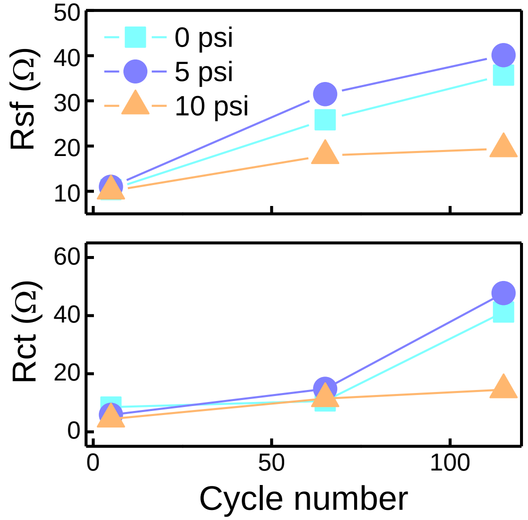


- A high-nickel, cobalt-free layered oxide (NMA) has been synthesized and benchmarked against NMC, NCA, and NMCAM of identical Ni content. High-Ni NMA delivers high specific capacity, long cycle life, and enhanced safety

CALCINATION PRESSURE EFFECT ON $LiNiO_2$



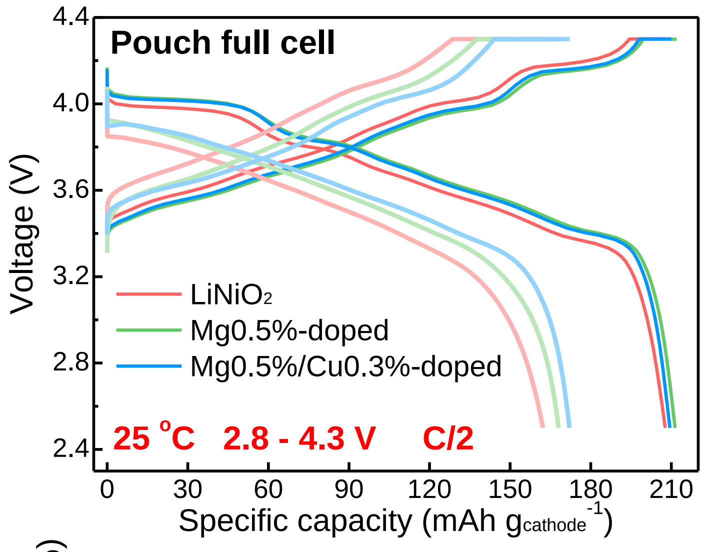


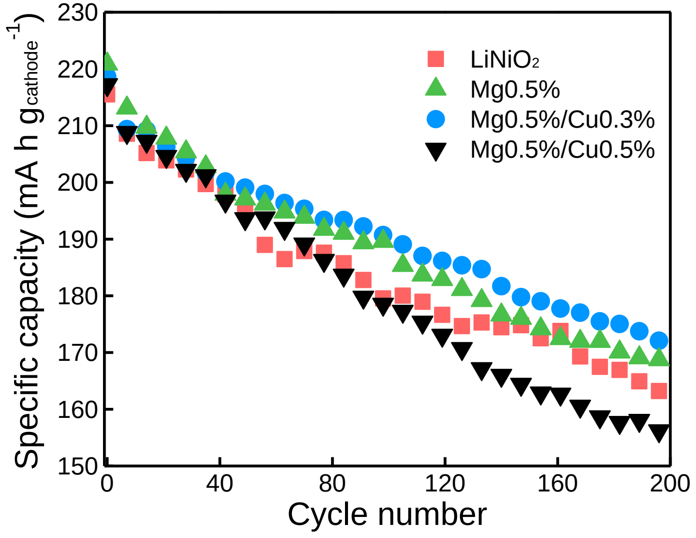


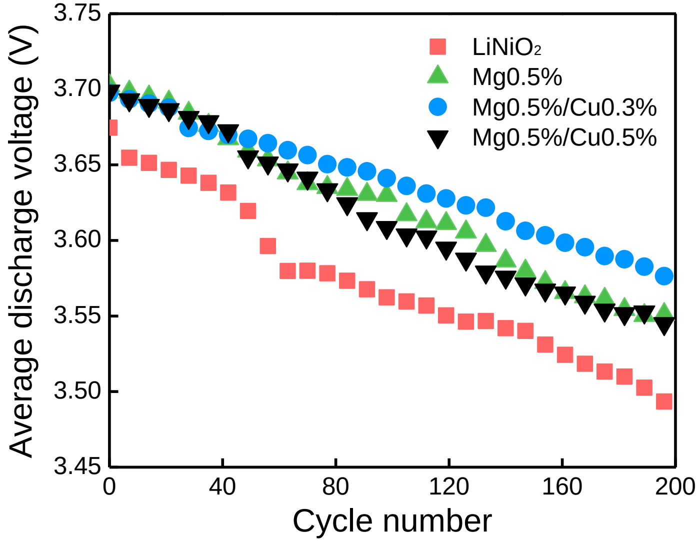
Furnace oxygen pressure	Li/Ni mixing	600th cycle capacity retention
0 psi	3.5%	70%
5 psi	3.2%	79%
10 psi	2.7%	81%

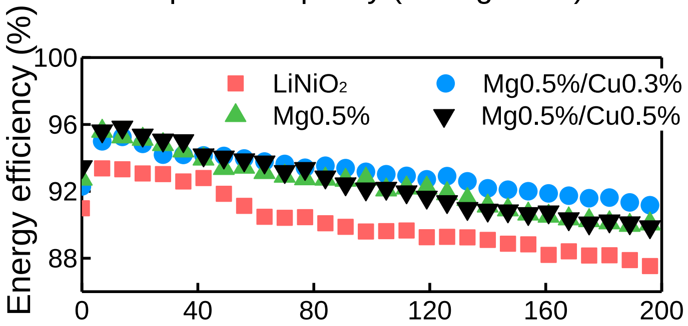
- $LiNiO_2$ synthesized in a pressurized oxygen environment shows improved cycle stability over $LiNiO_2$ synthesized under unpressurized oxygen
- Li^+/Ni^{2+} disorder is reduced with increasing calcination pressure
- Substantially reduced impedance growth in $LiNiO_2$ synthesized under 10 psi O_2 atmosphere
- Superior rate performance in 10 psi sample over control and 5 psi samples
- Changes in the structural and electrochemical properties of higher pressure samples are consistent with reduced oxygen vacancy concentration and cation disorder

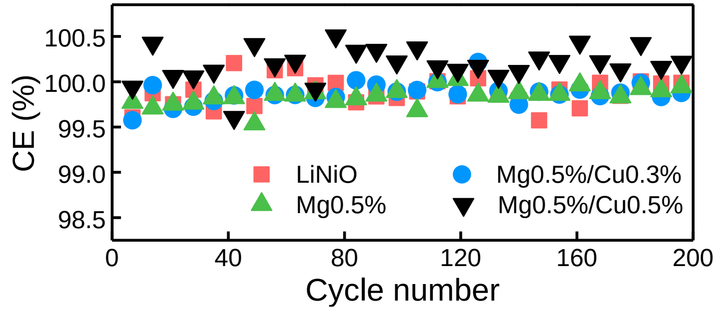
ELEMENTAL DOPING IN $LiNiO_2$











- A co-doping of Mg and Cu in $LiNiO_2$ improves cycle stability and energy efficiency with reduced polarization growth
- Removal of surface Li_2CO_3 by doping plays a critical role in improving the full-cell performance
- Co-doping with only as small as 0.3% Cu is much more effective in improving the electrochemical performance, while maintaining a robust crystal structure

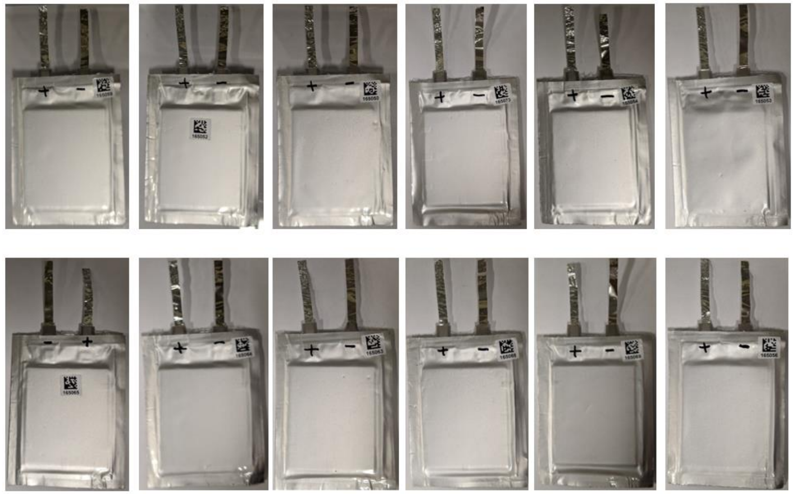
COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

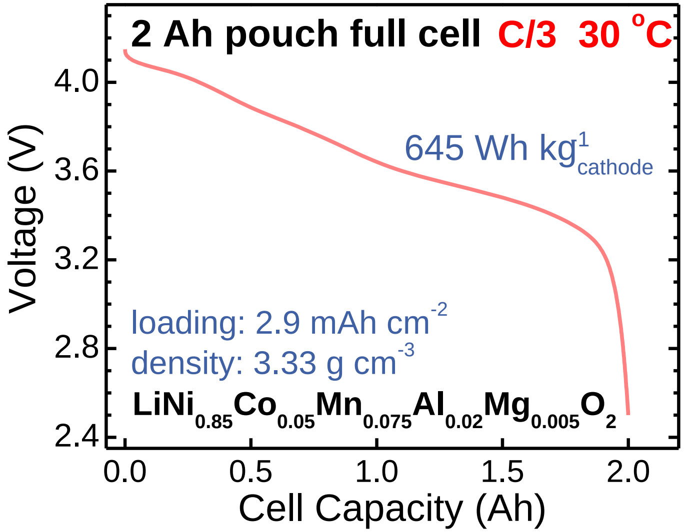
- Dr. Shriram Santhanagopalan, Nation Renewable Energy Laboratory (NREL)

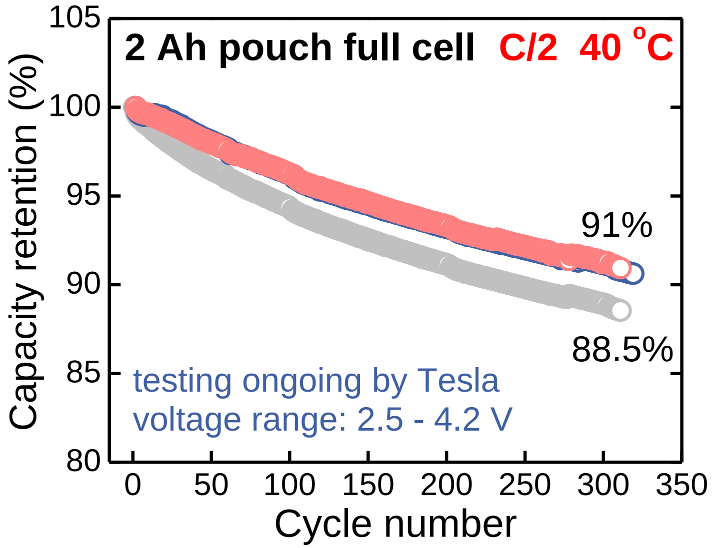
  Electrochemical testing and ALD coating exploration of high-nickel, low-/zero-cobalt cathode samples (*e.g*., NC-9406 and doped NMA-900505) supplied by UT Austin

- Dr. Hieu Duong, Tesla Inc.

  Fabrication of 2 Ah pouch full cells with a high-nickel, low-cobalt cathode ($LiNi_{0.85}Co_{0.05}Mn_{0.075}Al_{0.02}Mg_{0.005}O_2$) supplied by UT Austin







PROPOSED FUTURE RESEARCH

- FY2020
  - A survey of $LiNi_{1-x-y}Co_yM_xO_2$ ($y \le 0.05$ and $x \le 0.15$, M = Mn, Al, Mg, and more) and the effects of dopants on electrochemical performance, air-storage stability, and safety
  - High electrode loading and calendaring effects on the electrochemical performance of low-cobalt and cobalt-free compositions
  - Further evaluation and validation of ALD coatings by NERL on best-performing $LiNi_{1-x-y}Co_yM_xO_2$ ($y \le 0.05$ and $x \le 0.15$, M = Mn, Al, Mg, and more)
- FY2021
  - A survey of $LiNi_{1-x}M_xO_2$ ($x \le 0.20$, M = Mn, Al, Mg, and more) and the effects of dopants on electrochemical performance, air-storage stability, and safety
  - A survey of functional electrolyte additives on best-performing low-cobalt $LiNi_{1-x-y}Co_yM_xO_2$ and cobalt-free $LiNi_{1-x}M_xO_2$ in EC-free electrolytes

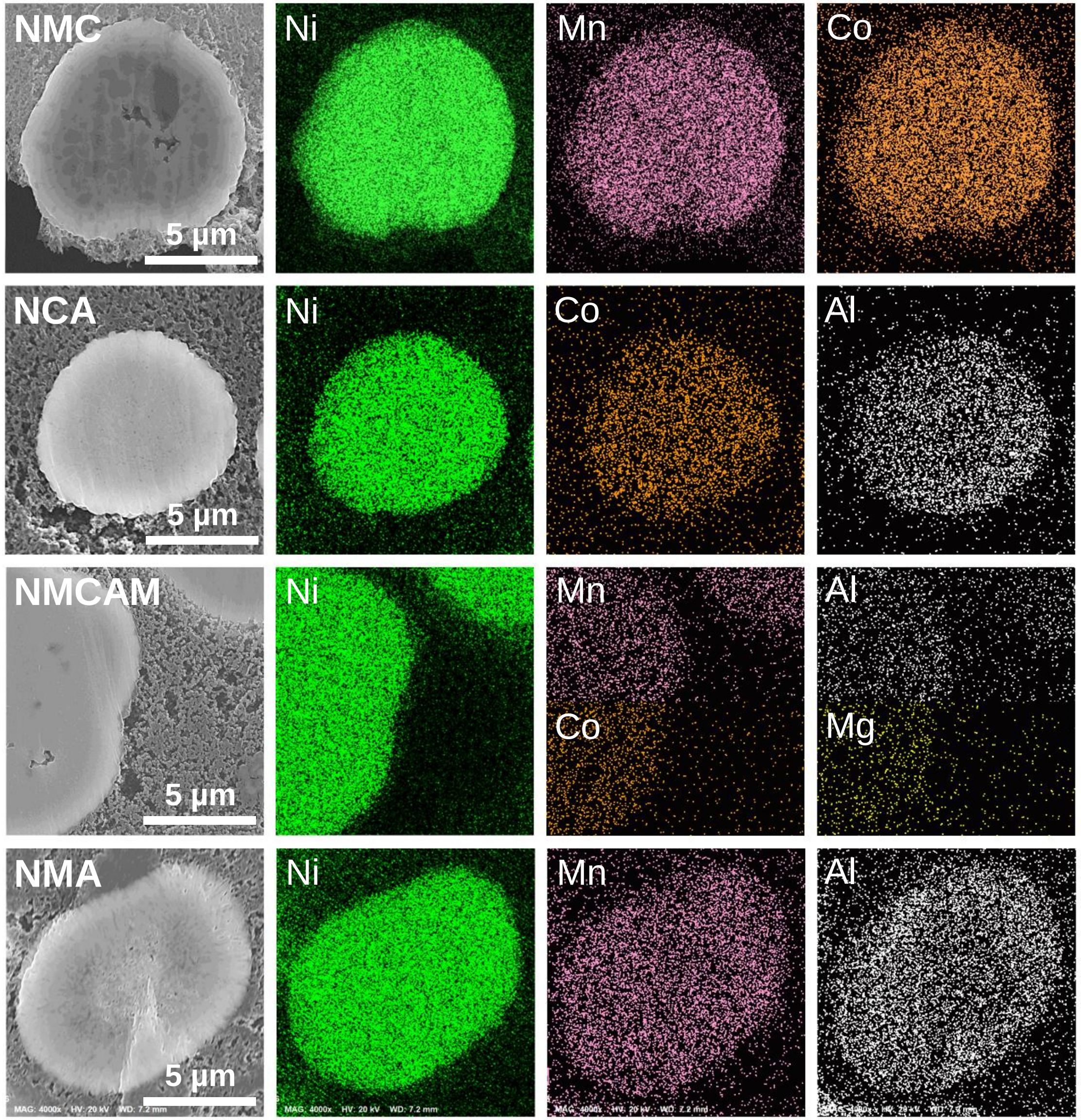
Any proposed future work is subject to change based on funding levels

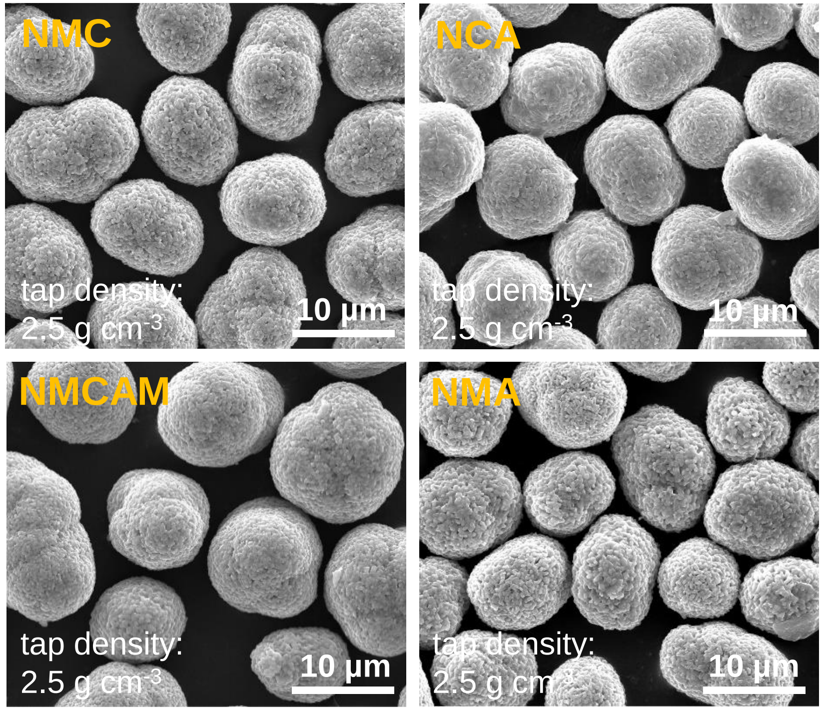
SUMMARY

- $Li[Ni_{1-x-y}Mn_xAl_y]O_2$ (NMA) demonstrates overall desired physical and electrochemical properties, including tap density, specific capacity, rate capability, cyclability, thermal stability, and residual Li compounds in comparison with $Li[Ni_{1-x-y}Mn_xCo_y]O_2$ (NMC), $Li[Ni_{1-x-y}Co_xAl_y]O_2$ (NCA), and $Li[Ni_{1-x-y-m-n}Mn_xCo_yAl_mMg_n]O_2$ (NMCAM)
- $LiNiO_2$ is known to be sensitive to synthesis conditions; with higher oxygen pressure in the furnace during calcination, $LiNiO_2$ shows enhanced rate capability and cyclability as well as suppressed cation (Li/Ni) mixing
- Co-doping with magnesium and copper enhances both the surface and bulk stability of $LiNiO_2$, improving energy efficiency and cyclability during cycling as well as air-storage stability
- A high-nickel, low-cobalt cathode sample ($LiNi_{0.85}Co_{0.05}Mn_{0.075}Al_{0.02}Mg_{0.005}]O_2$) delivered to Tesla for assembling 2 Ah pouch full cells shows good performance in rigorous commercial cell configurations. The cell testing is continuing at both Tesla and Idaho National Laboratory.

TECHNICAL BACKUP SLIDES

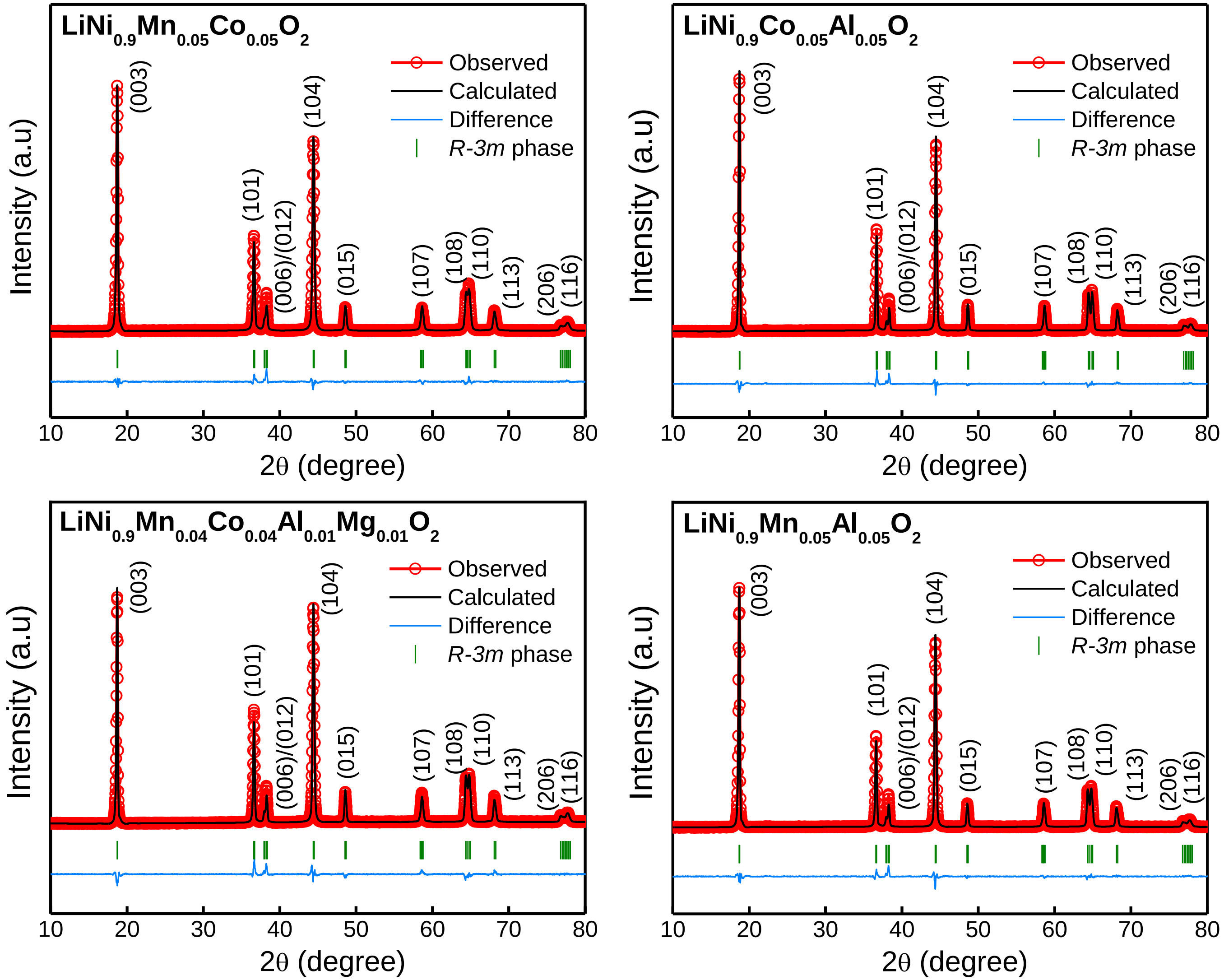
DESIGN OF HIGH-NICKEL, COBALT-FREE LAYERED CATHODES





- Four cathode samples (NMC, NCA, NMCAM, and NMA) consist of spherical particles of around 12 – 14 μm and SEM EDX shows uniform elemental distribution within a secondary particle, demonstrating high sample quality and consistency

DESIGN OF HIGH-NICKEL, COBALT-FREE LAYERED CATHODES

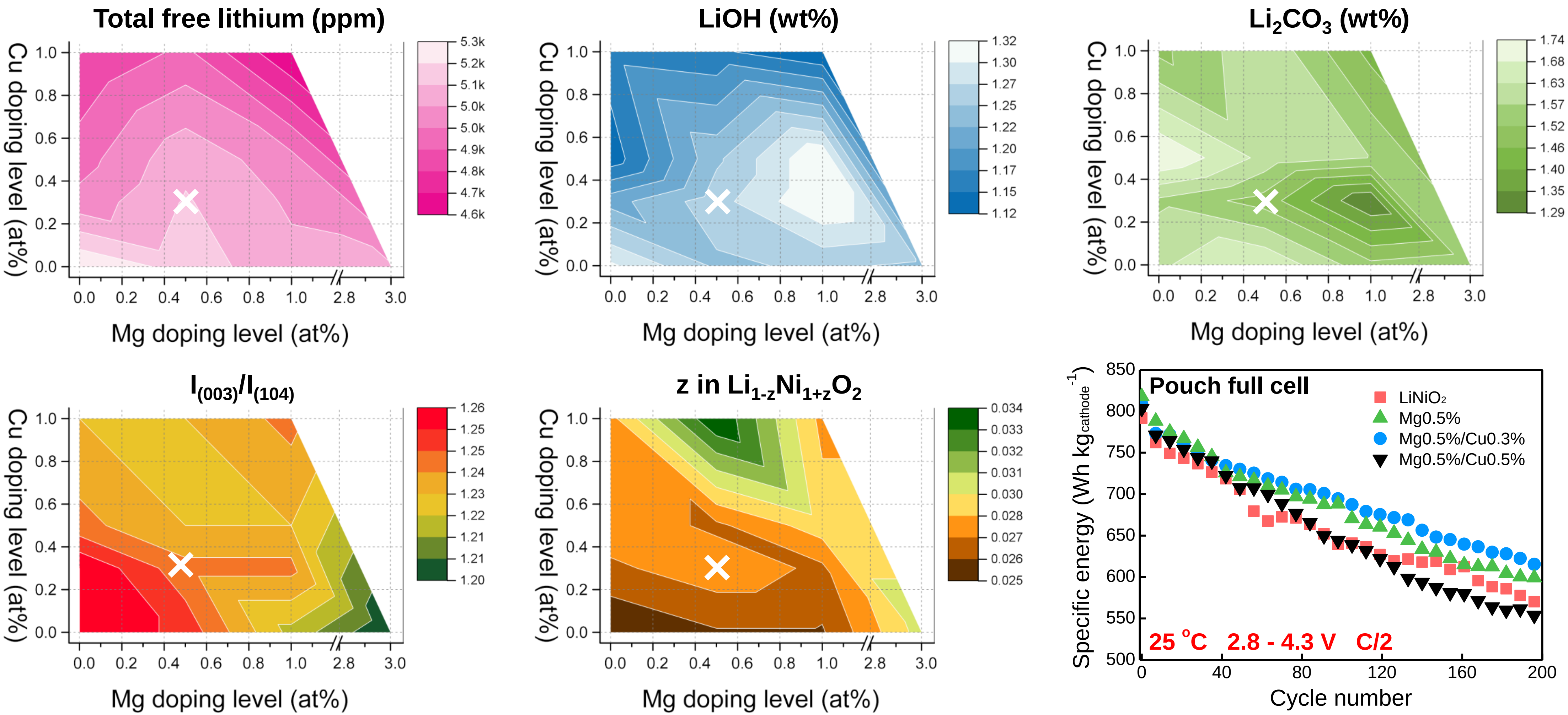


Precursors	Ni	Co	Mn	Al	Mg
NMC	0.890	0.055	0.055	0	0
NCA	0.883	0.053	0	0.064	0
NMCAM	0.890	0.042	0.044	0.013	0.011
NMA	0.883	0	0.056	0.061	0

Lithiated oxides	Li/Ni mixing	Residual Li
NMC	3.3%	2583 ppm
NCA	1.4%	2856 ppm
NMCAM	2.6%	2748 ppm
NMA	3.1%	2532 ppm

- Four cathode samples (NMC, NCA, NMCAM, and NMA) show consistent crystal structure. NMA shows relatively low surface residual lithium and reasonable level of Li/Ni mixing

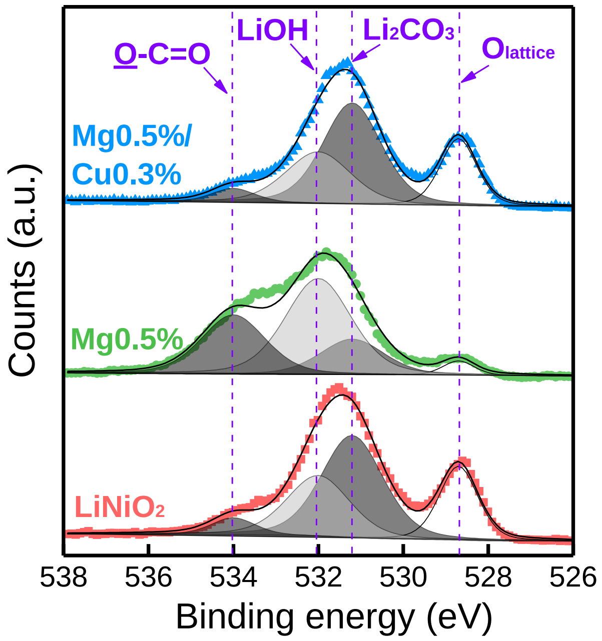
ELEMENTAL DOPING STUDY OF $LiNiO_2$



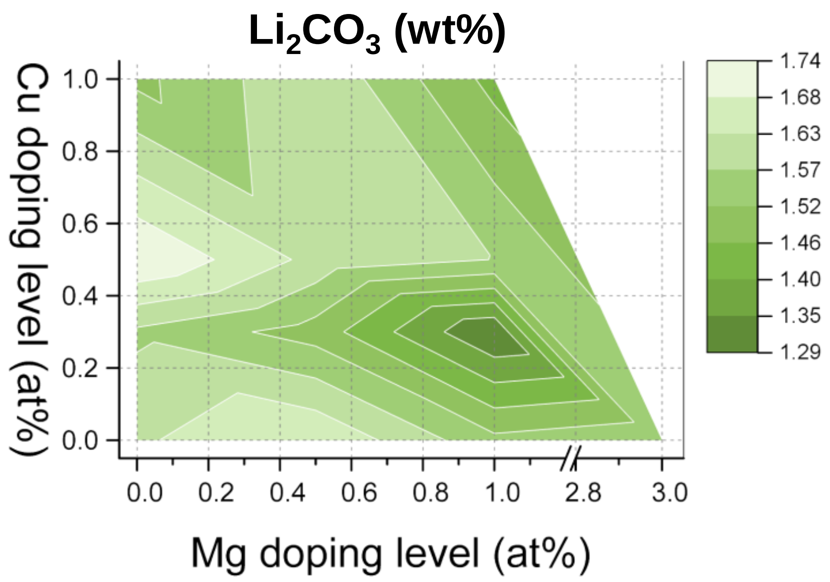
- Single Mg doping is not beneficial in terms of both surface and bulk properties of $LiNiO_2$
- The best full-cell stability is obtained when the amount of Li_2CO_3, not total free LiOH, is minimized with Cu doping

ELEMENTAL DOPING STUDY OF $LiNiO_2$

- Single magnesium doping rather deteriorated the surface stability of $LiNiO_2$
- Surface is stabilized by copper addition

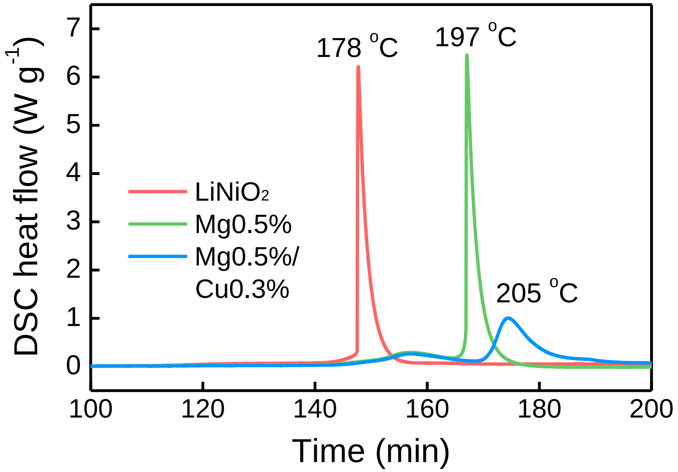


Cu

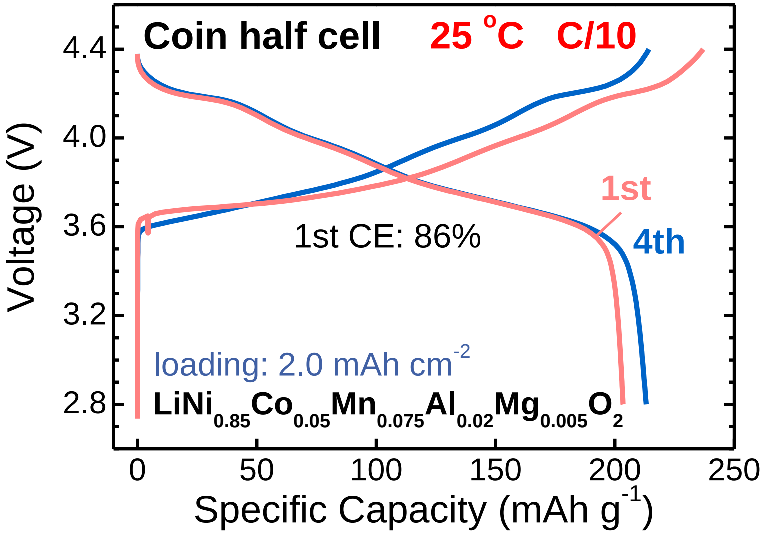


Mg

- TM-O bond stability is improved by either single or dual doping
- A synergy of bulk stability by Mg doping and surface stability by Cu addition is realized

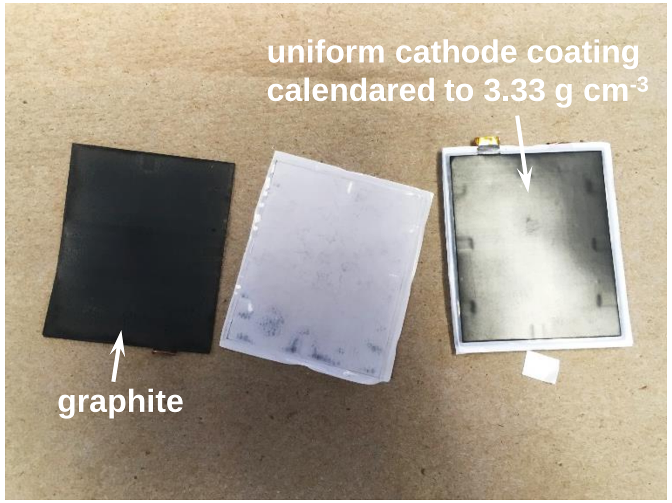


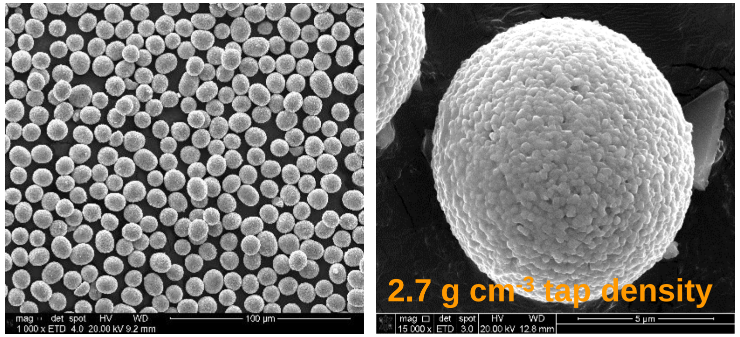
COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS



2 Ah cell cathode	
AC/carbon/binder	97/1/2 wt.%
Cathode loading	15.0 mg cm^{-2}
Areal capacity	2.9 mAh cm^{-2}
Density	3.33 g cm^{-3}
2 Ah cell anode	
AC/carbon/binder	97/1/2 wt.%
Anode loading	9.7 mg cm^{-2}
Areal capacity	3.3 mAh cm^{-2}
Density	1.49 g cm^{-3}

Cell metrics	
Weight	34.4 g
Cathode weight	33%
Electrolyte weight	16%
Volume (rough est.)	19.4 ml
Capacity (30 °C, C/3)	2.0 Ah
Voltage (30 °C, C/3)	3.65 V
Specific energy	215 Wh kg^{-1}
Energy density (rough est.)	376 Wh l^{-1}





- A high-Ni, low-Co cathode ($LiNi_{0.85}Co_{0.05}Mn_{0.075}Al_{0.02}Mg_{0.005}O_2$) was supplied to Tesla for assembling 2 Ah pouch cells in commercial cell configurations. These cells are being tested at both Tesla and INL